Renewable and Sustainable Energy Reviews 16 (2012) 1801–1816

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Thermo chemical conversion of biomass – Eco friendly energy routes

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ARTICLE INFO

Article history:
Received 25 April 2011
Accepted 6 January 2012
Available online 18 February 2012

Keywords:
Biomass
Thermo chemical
Gasification
Pyrolysis
Carbonization

ABSTRACT

Biomass is indirect source of solar energy and it is renewable in nature. It is one of the most important energy source in near future because of its extensive spread availability and promising potential to reduce global warming. Thermo chemical conversion of biomass yield variety of solid, liquid and gaseous fuels and have equal importance both at industrial and ecological point of views. Present review gives holistic view of various thermo-chemical conversion route of biomass. Gasification technology, pyrolysis options and scope of potential by product from there routes like hydrogen and charcoal production comprehensively reviewed with present context.

Contents

1. Introduction

Biomass store solar energy in the chemical form and it is most precious and versatile resources on earth. Biomass, unlike fossil fuels, is a renewable energy resource that is available where the climatic conditions are favorable for plant growth and production [1]. The term biomass is used for all organic materials which are combustible in nature, mainly plant and animal origin present in land and aquatic environments. Biomass includes by product and residue of crop farming and processing industries such as straw, husk, cobs, stalks, leaves, bark, fruits, cutting vines, in addition to animal refuses and plant products used in agro-industrial processing such as grains, bean, flower and some special products such as cassava, seaweeds [2–4]. Agricultural wastes particularly contain a high amount of organic constituents (cellulose, hemicellulose, lignin and minor amounts of other organics) and possess high energy content [5,6].

Biomass is considered carbon neutral, because the amount of carbon it can release is equivalent to the amount it absorbed during its life time. There is no net increase of carbon to the environment

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doi:10.1016/j.rser.2012.01.024

in the long term when combusting the lignocellulosic materials. Therefore, we can say that biomass is a renewable source of energy and can play vital role in responding to concerns over the protection of the environment and the security of energy supply [7,8].

Renewable technologies are considered as clean sources of energy and optimal use of these resources minimize environmental impacts, produce minimum secondary wastes and are sustainable based on current and future economic and social societal needs [9]. In the present context, it is considered a fuel source to partially replace the use of fossil fuels through thermo-chemical processes [10].

In this review paper an attempt has been made to identify the possible thermo chemical conversion routes of biomass. Energy harvested by means of this route is integrated with industrial applications to meeting their energy need. Possibilities of biomass gasification at industrial level, pyrolysis oil and their scope for transportation, applications of hydrogen in fuel cell, scope of charcoal production has also comprehensively presented in this paper.

2. Biomass classification

Biomass includes plantation that produces energy crops, natural vegetable growth and organic wastes and residues. This can be classified according to Panwar [11] and it is presented in Fig. 1. It can be grouped as:

(i). Agricultural & forestry residues: silviculture crops.
(ii). Herbaceous crops: weeds, Napier grass.
(iii). Aquatic and marine biomass: algae, water hyacinth, aquatic weeds, plants, sea grass beds, kelp and coral reef, etc.
(iv). Wastes: municipal solid waste, municipal sewage sludge, animal waste and industrial waste, etc.

3. Type of thermo chemical conversion route of biomass

Thermo chemical processes are most commonly employed for converting biomass into higher heating value fuels [12]. Major thermal conversion route is include direct combustion to provide heat, liquid fuel and other elements to generate process heat for thermal and electricity generation is summaries in Fig. 2.

3.1. Gasification

Biomass gasification is an efficient and environmentally friendly way to produce energy [13]. Gasification process is nothing but it is a conversion of solid fuel into gaseous fuel for wide applications. This whole process completed at elevated temperature range of 800–1300 °C [14] with series of chemical reaction that is why it come under thermo chemical conversion. Biomass as a feedstock is more promising than coal for gasification due to its low sulfur content and less reactive character. The biomass fuels are suitable for the highly energy efficient power generation cycles based on gasification technology. It is also found suitable for cogeneration. The combustion in gasifier takes place in limited supply of oxygen it may be called partial combustion of solid fuel [15]. The resulting gaseous product called producer gas is an energy rich mixture of combustible gas H_2, CO, CH_4 and other impurities such as CO_2, nitrogen, sulfur, alkali compounds and tars [16]. The chemical reaction during gasification process take place and constituents of producer gas is listed in Tables 1 and 2, respectively.

3.1.1. Classification of biomass gasifier's

Design of gasifier depends upon type of fuel used, air introduction in the fuel column and type of combustion bed as shown in Fig. 3.

Table 1
Basic gasification reactions [17].

Reaction	Heating value (kJ/mol)
$2C + O_2 \leftrightarrow 2CO$	+246.4
$C + O_2 \leftrightarrow CO_2$	+408.8
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	−206
$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	−165
$C + CO_2 \leftrightarrow 2CO$	−172
$C + H_2O \leftrightarrow CO + H_2$	−131

3.1.1.1. Fixed bed gasifiers. The fixed bed type gasifier simply consisting of cylindrical reactor in which solid biomass fuel gasifying and produced gas move either upward or downward. These types of gasifier are simple in construction and generally operate with high carbon conversion, long solid residence time; low gas velocity and low ash carry over [19]. Several type of fixed bed gasifiers were operating worldwide and further these can be classified according to the way in which primary air to gasify the biomass enters into the gasifier.

Updraft: As the name indicates, air is introduced at the bottom and biomass at top of the reactor. A metallic grate is provided at the bottom of the reactor which supports the reaction bed as shown in Fig. 4(a). Complete combustion of char takes place at the bottom of the bed, liberating CO_2 and H_2O. These hot gases (~1000 °C) pass through the bed above, where they are reduced to H_2 and CO and cooled to 750 °C. Continuing up the reactor, the reducing gases (H_2 and CO) pyrolyze the descending dry biomass and finally dry the incoming wet biomass, leaving the reactor at a low temperature (~500 °C). The gas is drawn at upper side. Producer gas contain more tar therefore it not recommended for engine applications. It is found most suitable for thermal applications. If it operates with fuel like charcoal, product gas can be used for motive power generation after cleaning and cooling [20].

Downdraft: This type of gasifier found most suitable to convert high volatile fuel (wood, biomass) to low tar gas and therefore most suitable design for power generation. In this type of gasifier, air is introduced into downward flowing packed bed or solid fuels and gas is drawn off at the bottom (see Fig. 4b).

Crossdraft gasifier: Crossdraft gasifier suitable for low ash fuels such as wood, charcoal and coke. The load following ability of crossdraft gasifier is quite good due to concentrate partial zone which operates at temperatures up to 2000 °C. Start up time (5–10 min) is much faster than that of, this type of gasifier such as downdraft and updraft units [21]. The relatively higher temperature in cross draft gas producer has an obvious effect on gas composition such as high carbon monoxide, and low hydrogen and methane content when dry fuel such as charcoal is used (see Fig. 4c).

Fluidized bed gasifier: Fluidized bed (FB) gasification has been used extensively for coal gasification from many years, its advantage over fixed bed gasifiers being the uniform temperature distribution achieved in the gasification zone [22]. In this type

Table 2
Constituents of producer gas [18].

Compounds	Symbol	Gas (vol.%)	Dry gas (vol.%)
Carbon monoxide	CO	21.0	22.1
Carbon dioxide	CO_2	9.7	10.2
Hydrogen	H_2	14.5	15.2
Water vapour	H_2O	4.8	–
Methane	CH_4	1.6	1.7
Nitrogen	N_2	48.4	50.8
Gas high heating value			
Generator gas (wet basis)			5506 kJ/Nm^3
Generator gas (dry basis)			5800 kJ/Nm^3
Air ratio required for gasification			2.38 kg wood/kg air
Air ratio required for gas combustion			1.15 kg wood/kg air

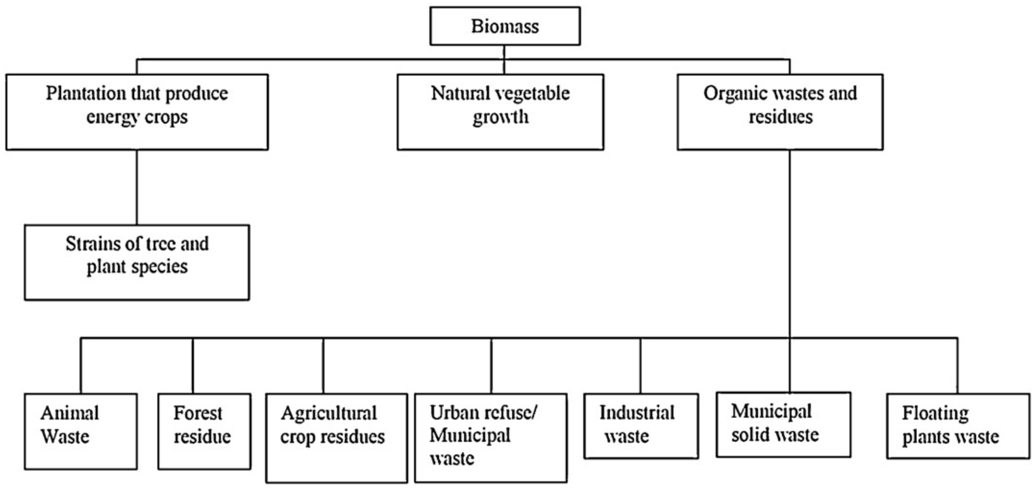


Fig. 1. Biomass classification.

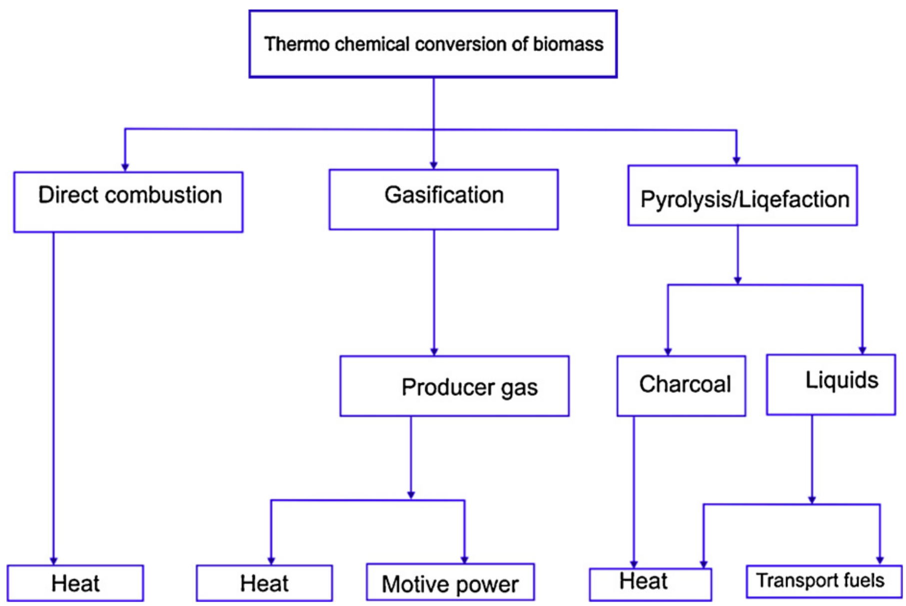


Fig. 2. Thermo chemical conversion route of biomass.

of gasifier, air is blown through a bed of solid particles at a sufficient velocity to keep these in a state of suspension. The bed is externally heated and the feedstock is introduced as soon as a sufficiently high temperature is reached. The fuel particles are introduced at the bottom of the reactor as shown in Fig. 5, very quickly mixed with the bed material and almost instantaneously heated up to the bed temperature. As a result of this treatment the fuel is pyrolyzed very fast, resulting in a component mix with a

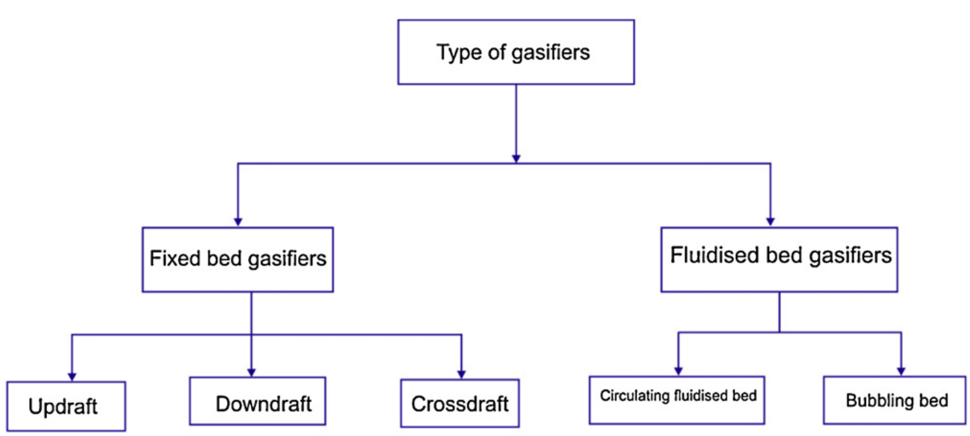


Fig. 3. Classification of gasifiers.

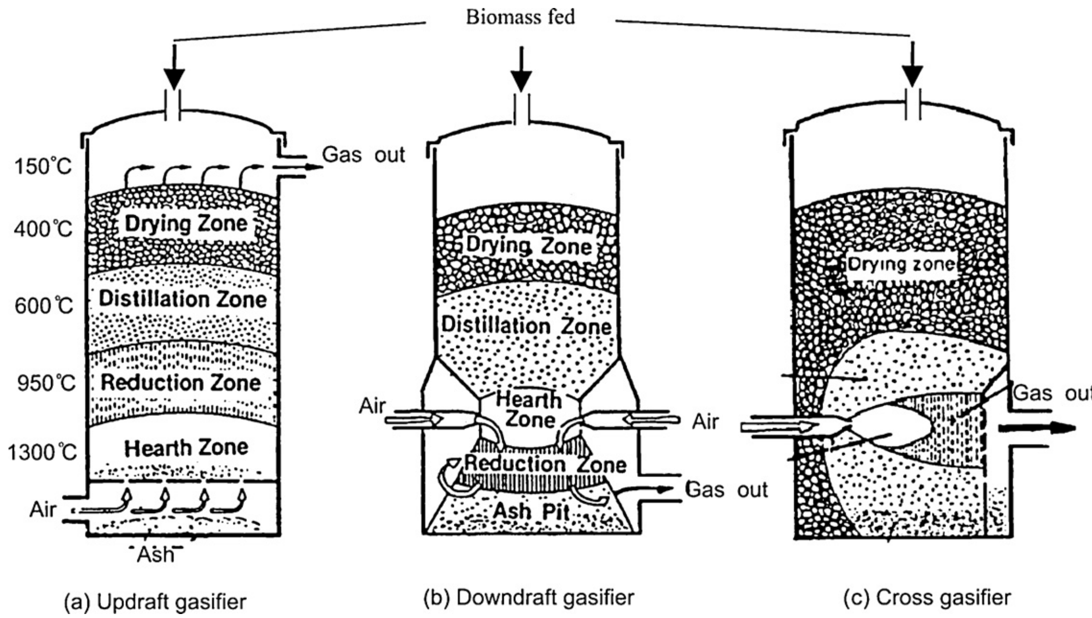


Fig. 4. Fixed bed gasifiers.

relatively large amount of gaseous materials. Further gasification and tar-conversion reactions occur in the gas phase. Most systems are equipped with an internal cyclone in order to minimize char blow-out as much as possible. Ash particles are also carried over the top of the reactor and have to be removed from the gas stream if the gas is used in engine applications.

3.1.2. Design of gasifier

Its design is based on energy requirement and it can be completed with following steps [24]:

(i) Feed stock consumption rate

$$\text{Feed stock consumption rate} = \frac{\text{Gas output} \times \text{Calorific value of gas}}{\text{Hot gas efficiency} \times \text{Calorific value of feedstock}}$$

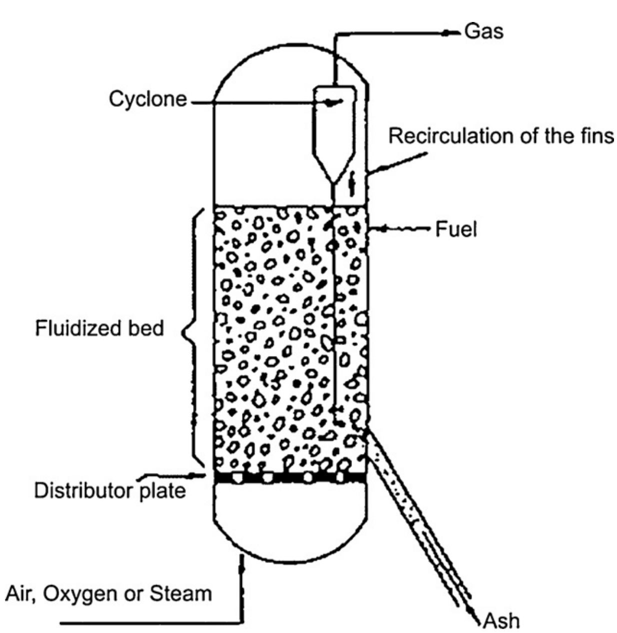


Fig. 5. Fluidized bed gasifier [23].

(ii) Dimension of the reactor shell

$$\text{Reactor cross sectionalarea} = \frac{\text{Feed stock consumption rate}}{\text{Specific gasification rate}}$$

(iii) Height of the reactor

$$\text{Volume occupied by wood chip} = \frac{\text{Holding capacity}}{\text{Bulk density of wood chips}}$$

$$\text{Height ofwood chips holding column} = \frac{\text{Volume occupied by wood chips}}{\text{Reactor cross sectional area}}$$

3.1.3. Case studies

There are number of gasifiers has been installed at industrial site for actual use. Some of them is studied and presented here:

Gordillo and Belghit [25] develop a numerical model for solar downdraft gasifier to gasifying biomass char (biochar) with steam. The model found that the system efficiency could be as high as 55% for small steam velocities, energy conversion efficiency decreases when the steam velocity is increased and when the bed is heated quickly. They concluded from the model that the downdraft set-up could be a great solution in order to improve the performance of the packed bed and fluidized bed gasifiers with concentrated solar radiation in the upper side of the reactor. The gas produced is a high quality syngas, in which the H_2 is the principal component followed by CO; the CO_2 yield is small because no combustion is conducted.

An experimental investigation was conducted by Dogru et al. [26] to assess gasification potential of hazelnut shells. The experimental setup used for experiments is illustrated in Fig. 6. They were reported that the optimum operation of the gasifier is found to be between 1.44 and 1.47 Nm^3/kg of air fuel ratios at the values of 4.06 and 4.48 kg/h of wet feed rate which produces the producer gas with a good Gross Calorific Value of about 5 MJ/m^3 at a volumetric flow of 8–9 N m^3/h product gas. The gasifier produces low tar and char at a ratio of 0.005 and 0.051 of the feed, respectively. It was concluded that hazelnut shells could be easily gasified in a downdraft gasifier to produce good quality gas with minimum polluting by-products. They were suggested that, in view of ease

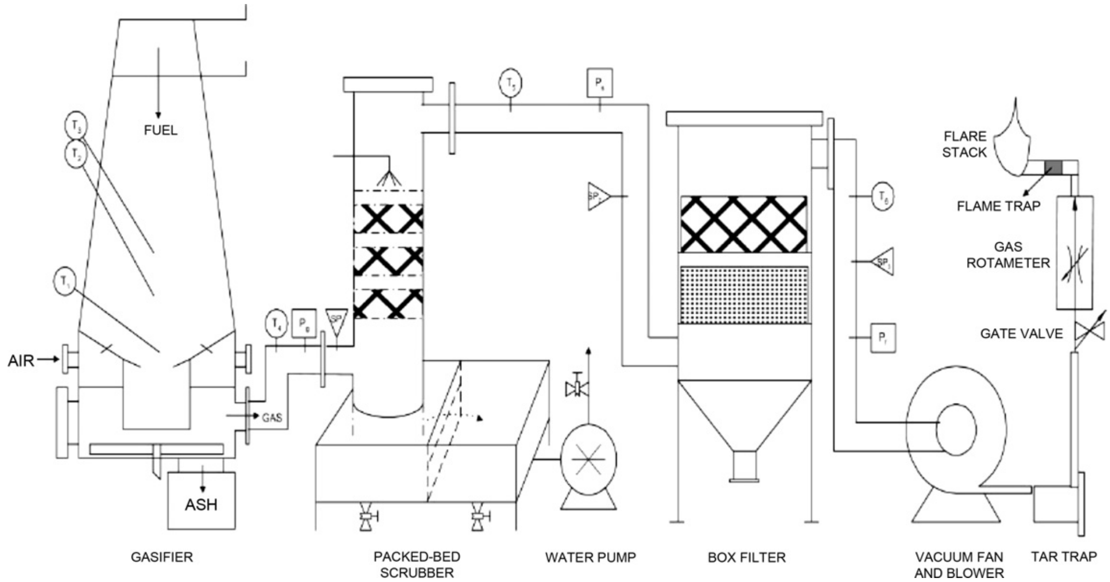


Fig. 6. Schematic of the experimental.

of operation, small-scale gasifiers can make an important contribution to the economy of rural areas where the residues of nuts are abundant. It was also suggested that gasification of shell waste products is a clean alternative to fossil fuels and the product gas can be directly used in internal gas combustion engines.

In the same fashion an experimental study on downdraft gasifier at food processing industry was conducted by Panwar et al. [27]. Initially the industry was operated with liquefy petroleum gas (LPG) as fuel. Their experiment reveals that 6.5 kg of LPG is fully replaced by 38 kg of sized wood on hourly basis. The maximum temperature of the oven at no load attained was 367 °C in 130 min at 100.7 $Nm^3\,h^{-1}$ gas flow rate. This system has resulted a saving of about 19.5 tons of LPG over 3000 h of operation, implying a saving of about 33 tons of CO_2 emission, thus a promising candidate for clean development mechanism. Fuel economic analysis of gasifier system showed that the saving was about 13,850 US$ for 3000 h of baking operation.

Rathore et al. [28] installed an open core downdraft type biomass gasifier at M/S Phosphate India Pvt. Ltd., Udaipur for heating and concentrating phosphoric acid. The installed gasifier consumes 100–120 kg/h of sized wood and calorific value of producer gas was recorded as 4.35 $MJ\,Nm^{-3}$. They were reported that gasifier system perform constantly well in industries for thermal application which not only a means of energy conservation, but also there is huge scope to conserve fossil fuel and reduction in greenhouse gases as well.

An experimental investigation on down draft biomass gasifier was carried out with woody and densified fuel by Panwar [29]. The gasifier having 180 kWth capacity and it was reported that densified fuel satisfactorily gasifies. The gasifier performance with different fuels shows that the calorific value of producer gas varied in the range of 4.3–4.8 $MJ\,m^{-3}$ and cold gas efficiency in the range of 66–73%. The flame temperatures of the producer gas for all feed stocks varied in the range of 750–857 °C. The gasifier used for study at industrial site is illustrated in Fig. 7. The study showed that there was a flow problem with densified fuel. To overcome this problem, scheduled ramming or pocking is recommended. A saving of around 23.58 US$ per day of fuel capacity operation is being effected on fuel and carbon credited in additional benefit.

Jaojaruek et al. [30] conducted experiments on three different downdraft gasification approaches: single stage, conventional two-stage, and an innovative two-stage air and premixed air/gas supply approach. They partially bypassed producer gas to mix with air and supplied to burn at the pyrolysis zone and it was observed that producer gas quality generated by the innovative two-stage approach significantly improved as compared to conventional two-stage. The higher heating value (HHV) increased from 5.4 to 6.5 MJ/Nm^3. Tar content in producer gas reduced to less than 45 mg/Nm^3. With this approach, gas can be fed directly to an internal combustion engine. There was considerable improvement in gasification thermal efficiency and it increased by approximately 14%. This novel approach yield double benefits on gas quality and energy savings.

An experimental investigation of a downdraft biomass gasifier was carried out using furniture wood and wood chips by Zainal et al. [31]. The experimental setup of system is presented in Fig. 8. They reported that the calorific value of the producer gas increases with equivalence ratio initially, attains a peak and then decreases with the increase in equivalence ratio. It was also observed that complete conversion of carbon to gaseous fuel has not taken place even for the optimum equivalence ratio. The cold gas efficiency of the biomass gasifier was found in the order of about 80% whereas the overall efficiency of the biomass electrical power producing system is of the order of 10–11%. The specific consumption of the biomass material is found to be of the order of 2 kg/kW h.



Fig. 7. Experimental gasifier at industrial site.

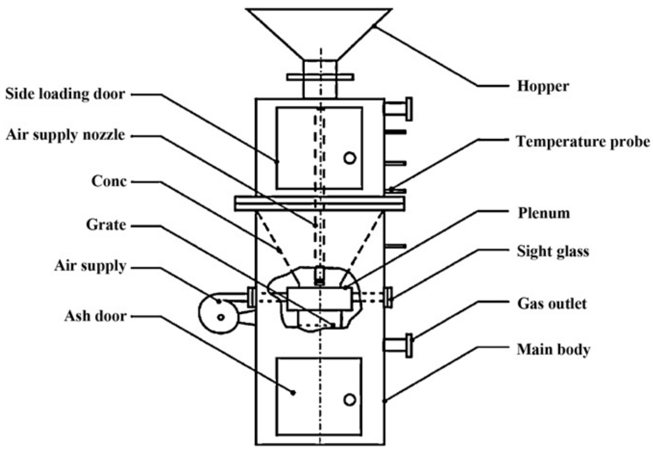


Fig. 8. Experimental set-up of the gasifier.



Fig. 9. A view of 75 kWth, downdraft biomass gasifier.

Similarly Sheth and Babu [32] investigate the performance of downdraft gasifier using waste generated while making furniture. Dalbergia sisoo, generally known as sesame wood or rose wood is mainly used in the furniture and wastage of the same was used as a feed stock for experimental study. On the basis of their results they reported that an increase in the moisture content, biomass consumption rate decreases and with an increase in the air flow rate biomass consumption rate increases. The calorific value, pyrolysis zone temperature and the oxidation zone temperature maximum at equivalence ratio (ϕ) = 0.205. However, the calorific value decreases for an equivalence ratio ranging from 0.205 to 0.35. It was also concluded that the value of cold gas efficiency was 0.25 for ϕ = 0.17. It becomes almost double with a small increase of 0.035 in the value of ϕ. The effect of ϕ on cold gas efficiency is comparatively lower for higher values of ϕ.

Sharma [33] conducted experimental study on a 75 kWth (see Fig. 9), downdraft biomass gasifier to assess temperature profile, gas composition, calorific value and trends for pressure drop across the porous gasifier bed, cooling–cleaning train and across the system as a whole in both firing as well as non-firing mode. It was found that the pressure drop across the porous bed, cooling–cleaning train, and spray coolers is found to be sensitive to the increase in flow rate, while the sand bed filters is found to be a strong function of quartz particle size in addition to the flow rate through them. The tar/particulate deposited over the quartz particles constituting the filter bed gives comparatively higher pressure drop across them. To overcome from this pressure drop problem regular shaking of grate is essential before a certain interval. In firing mode, the higher temperature in bed tends to better conversion of non-combustibles component (like CO_2, H_2O) into combustible component (like CO, H_2) in the resulting gas and, thus, improves in the calorific value of product gas. Any increase in temperature in bed either due to energetic of reactions or any other reason like increase in gas flow rates tends to higher resistance to flow through the porous bed and thus higher pressure drops.

Garcıa-Bacaicoa et al. [34] investigate the thermal decomposition behavior of mixtures of wood particles and high density polyethylene (HDPE) in different atmospheres conditions in a downdraft gasifier having fuel consumption capacity of 50 kg/h. An experimental layout is illustrated in Fig. 10. In order to do so, experiments were conducted with biomass only and with mixtures up to 15% HDPE. They reported that the main components of the gas generated were N_2 (50%), H_2 (14%), CO (9–22%) and CO_2 (7–17%) and its relatively high calorific value was adequate for using it in an internal combustion engine generator consisting of a modified diesel engine coupled with a 25 kVA alternator.

Open core down draft gasifier burner system having capacity 1.25 GJ/h, suitable for thermal application was installed at M/s Dinesh Pharmaceutical Pvt. Ltd., Nandesari, for steam generation by Sardar Patel Renewable Energy Research Institute (SPRERI) as shown in Fig. 11 [35]. Producer gas burner was used in dual fuel mode (60% LDO (light diesel oil) + 40% producer gas). It was reported that installed gasifier consumed 78–80 kg/h of wood and replaced 40% (20 l per hour) LDO. The system was tested for a cumulative

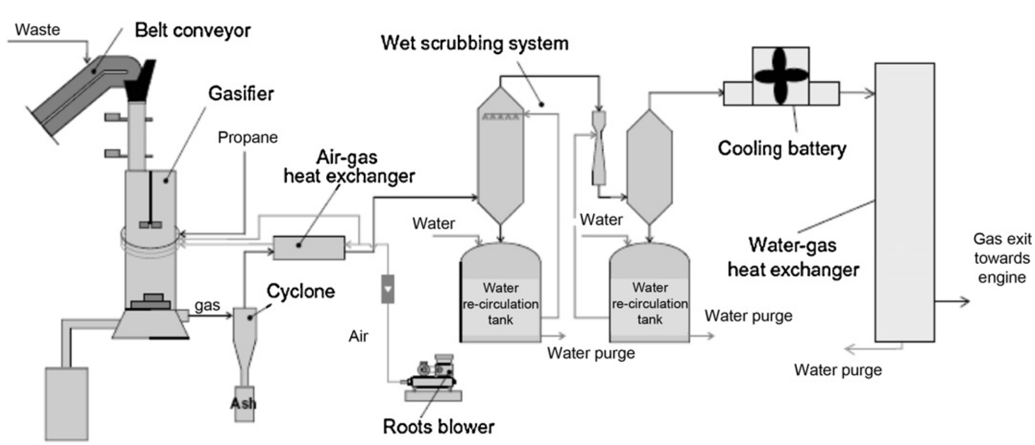


Fig. 10. Experimental layout of biomass/HDPE mixtures downdraft gasifier.



Fig. 11. Gasifier system for steam generation installed at Dinesh Pharmaceutical Pvt. Ltd., Nandesari.

period of 600 h using sawmill woody waste as feedstock in test runs of 15–18 h. The system was in position to save about Rs. 221.8 per hour by using dual fuel (60% LDO + 40% producer gas) for steam generation.

Package of practice was developed by IISc, Banglore to dry marigold flower with open top downdraft gasifier. The developed gasifier is in position to replaces 2000 l of diesel or LDO per day completely. The system operates over 140 h per week on a nearly nonstop mode and over 4000 h of operation replacing fossil fuel completely [36].

There are number of electricity power generation units operating with biomass as primary fuel. Turnbull [37] studied 46 such power plants working in central and northern California using wood wastes and/or agricultural residues to fire steam turbines. The plants are fueled by sawdust or pulp process wastes, hog fuel, in-forest thinning, clean land filled wood, orchard and vineyard wastes, and other agricultural residues. The smallest plant provides less than 3 MW of power to the utility grid and the largest nearly 50 MW. Overall they consume more than 7 million bone dry tons (BDT) of fuel each year, using about 1 BDT to generate 1 MW h, an overall efficiency of about 20%.

Integrating gasifiers with gas turbines is not a new technique. It makes possible to achieve high efficiencies and low unit capital costs in modest-scale biomass power generating utility. Electricity produced with biomass-integrated gasifier/gas turbine (BIG/GT) power systems would be competitive with electricity produced from coal and nuclear energy under a wide range of circumstances. Biomass also offers major environmental benefits. Initial applications will be with biomass residues generated in agro- and forest-product industries. Eventually, energy plantation is required to run the power station for long terms [38].

A comprehensive study on economic performance, CO_2 emissions and energy use with biomass integrated gasification combined cycle (BIGCC) for pulp and paper production industry as shown in Fig. 12 was conducted by Wetterlund et al. [39]. The BIGCC cases study show a consistent potential to reduce the primary energy use, due to the substantial decrease in demand for marginal electricity. If the marginal electricity production is high emitting (coal power), this also leads to a decrease in global CO_2 emissions. Finally, they concluded that if the aim is to implement biomass gasification in pulp and paper production as a means to meet both economic and environmental objectives, biomass gasification for electricity production could provide a more robust solution than gasification for biofuel production.

Patil et al. [40] installed a natural draft gasifier at a ceramic industry to replace the use of light oil in ceramic drying. The rated capacity of gasifier was about 350 kWth and consume about 80 kg/h of sawmill residues and it in position to save about 17 l of fuel oil per hour. They reported that biomass conversion efficiency was 78% and flame temperature around 1000 °C. In the same fashion a study on updraft type gasifier for thermal application was conducted by Sharma and Panwar [41]. They tested the system over a cumulative period of about 30 h and found flame temperature in the range of 298–642 °C. The overall thermal efficiency of the system was around 39.53%. The techno economic parameters, i.e., net present worth, benefit cost ratio and pay back period were also analyzed and it was found to be Rs. 4,41,987; 2.11 years and 3.5 years, respectively.

There is massive possibility to utilize producer gas to generate process heat or motive power generation but special attention to be paid for proper combustion of producer gas. In this regard premixed type producer gas burner was designed and its performance was evaluated by Panwar et al. [42]. The developed burner couple with downdraft type biomass gasifier as shown in Fig. 13. They studied emission characteristics and found low NO_x and CO emission at 125 $Nm^3 h^{-1}$ as compared to that of 75 and 100 $Nm^3 h^{-1}$. Maximum flame temperature (753 °C) was recorded at of 10 cm axial and 10 mm radial distance.

Biomass gasification to generate raw syngas used in anaerobic fermentation processes is one of several emerging technologies for the production of biofuels from biomass. The gasification–fermentation process can utilize a wide variety of lignocellulosic biomass such as prairie grasses, wood chips, and paper

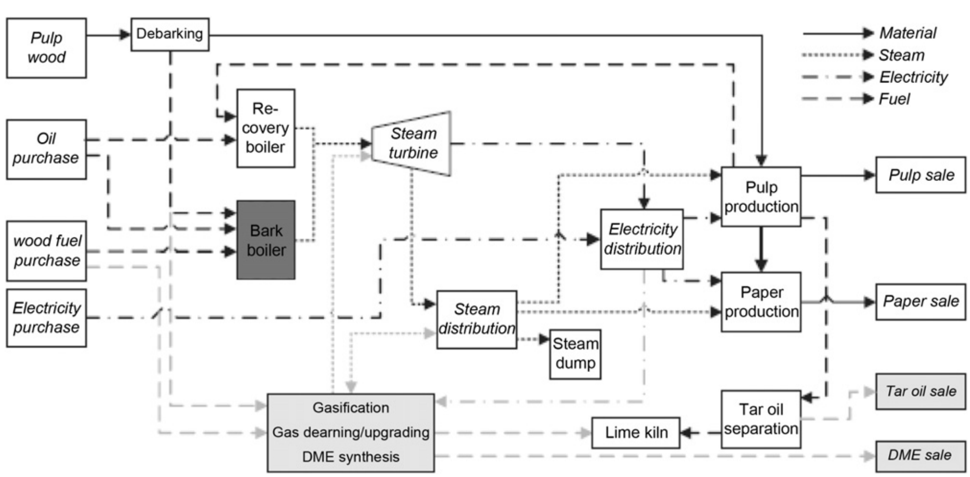


Fig. 12. Biomass integrated gasification combined cycle (BIGCC) for pulp and paper production industry.

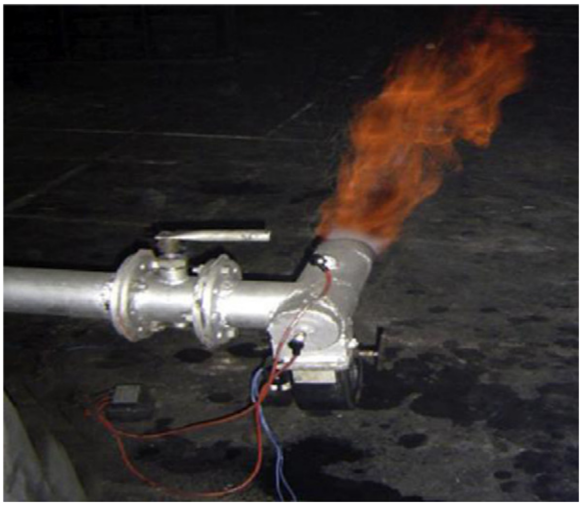


Fig. 13. Produce gas burner.

wastes, in addition to non-lignocellulosic biomass such as solid municipal wastes [43].

In the present context combination of biomass gasification with solid oxide fuel cells (SOFCs) is achieving more research interest as an efficient and environmentally benign method of producing electricity and process heat [44]. Similar concept was proposed with biomass integrated gasification fuel cell by Nagel et al. [45].

High temperature plasma gasification deems efficient energy ladder because of plasma by comparison with existing thermo chemical processes are in the high heating value gases, process control and the lower energy consumption per unit of output. From one kilogram of 20% moisture wood it is possible to obtain 4.6–4.8 MJ of electricity (net of electricity input) and 9.1–9.3 MJ of thermal energy when using wood with average elemental composition and with a LHV energy content of 13.9 MJ, when using a combined Brayton and Steam cycle generating plant. An air plasma gasification plant using alternating current (AC) plasma torches was integrated with a thermodynamic model showing that the chemical energy in the produced syngas was 13.8–14.3 MJ/kg with a power input of 2.2–3.3 MJ/kg [46].

3.2. Pyrolysis of biomass

Pyrolysis of biomass is generally categorized under thermo chemical conversion process [47]. Although pyrolysis is still in the developing stage but looking toward present energy scenario, pyrolysis has received special attention as it can convert biomass directly into solid (charcoal), liquid (bio oil), and gaseous (fuel gas) products by thermal decomposition of biomass in the absence of oxygen [48,49].

Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by pyrolysis. In the 1980s, researchers found that the pyrolysis liquid yield could be increased using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly [50]. It is the heart of all thermo-chemical fuel conversion processes and become an avenue to produce petroleum like products from biomass. Pyrolytic oil may be used directly as a liquid fuel for boiler, diesel engine, gas turbine for heat and electricity generation, or catalytically upgraded to transport grade fuels [51,52]. In all thermo-chemical conversion processes, pyrolysis plays a key role in the reaction kinetics and hence in reactor design and determining product distribution, composition, and properties [53].

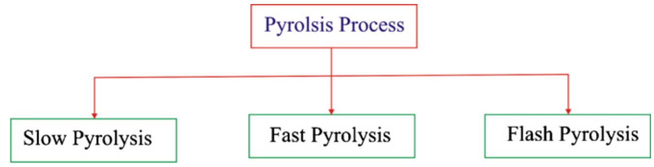


Fig. 14. Type of pyrolysis process.

In wood derived pyrolysis oil, specific oxygenated compounds are present in relatively large amounts [50,54,55]. Rapid heating and rapid quenching produced the intermediate pyrolysis liquid products, which condense before further reactions break down higher molecular-weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed [56]. The main pyrolysis variants are listed in Table 3.

3.2.1. Classification of pyrolysis process

Pyrolysis process broadly classified on the basis of operation conditions and its classification is depicted in Fig. 14. Quality and quantity of resulting products obtained from biomass pyrolysis depend mainly on the chemical composition of the feedstock and the operating temperature [58].

3.2.1.1. Slow pyrolysis. Slow pyrolysis is well known and usually appears in traditional charcoal kiln. Slow pyrolysis of biomass is associated with high charcoal continent [59]. Operating temperature in slow pyrolysis process usually in the range of 550–950 K.

3.2.1.2. Fast pyrolysis. In the fast pyrolysis process biomass is thermolys at elevated temperature (577–977 °C) in the inert atmospheric conditions. Yield of fast pyrolysis processes is 60–75 wt.% of liquid bio-oil, 15–25 wt.% of solid char, and 10–20 wt.% of non-condensable gases, depending on the feedstock used [50]. Essential features of a fast pyrolysis process can be categorized in four groups [50,59,60]: (1) very high heating and heat transfer rates are used, which usually requires a finely ground biomass feed, (2) a carefully controlled pyrolysis reaction temperature is used, often in the 700–775 K range, (3) short vapor residence times are used (typically <2 s), and (4) pyrolysis vapors and aerosols are rapidly cooled to give bio-oil. Fast pyrolysis process is illustrated in Fig. 15 [61].

3.2.1.3. Flash pyrolysis. This process use to produce petroleum equivalent biomass crude oil with high yield efficiency of up to 70% [62–64]. Refined crude oil can be used to generate heat or motive power generation. Operating temperature of flash pyrolysis is in the range of 777–1027 °C. Final product of this process

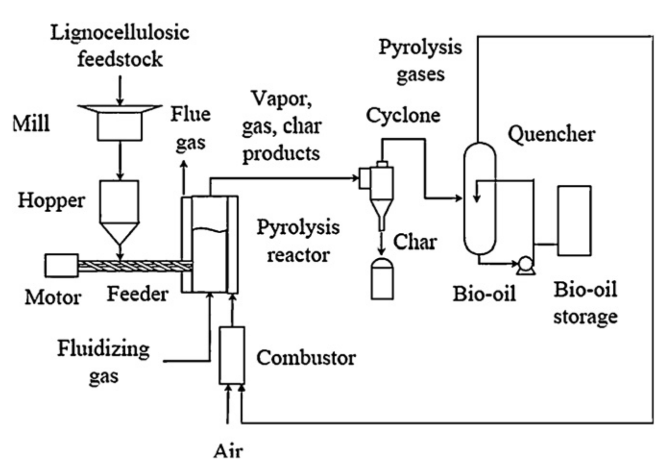


Fig. 15. Fast pyrolysis process layout.

Table 3
Pyrolysis methods and their variants [57].

Method	Residence time	Temperature (°C)	Heating rate	Products
Carbonation	Days	402	Very low	Charcoal
Conventional	5–30 min	602	Low	Oil, gas, char
Fast	0.5–5 s	925	Very high	Bio-oil
Flash-liquid[a]	<1 s	<652	High	Bio-oil
Flash-gas[b]	<1 s	<652	High	Chemicals, gas
Hydro-pyrolysis[c]	<10 s	<502	High	Bio-oil
Methano-pyrolysis[d]	<10 s	>702	High	Chemicals
Ultra pyrolysis[e]	<0.5 s	1002	Very high	Chemicals, gas
Vacuum pyrolysis	2–30 s	402	Medium	Bio-oil

[a] Flash-liquid: liquid obtained from flash pyrolysis accomplished in a time of <1 s.
[b] Flash-gas: gaseous material obtained from flash pyrolysis within a time of <1 s
[c] Hydropyrolysis: pyrolysis with water.
[d] Methanopyrolysis: pyrolysis with methanol.
[e] Ultra pyrolysis: pyrolysis with very high degradation rate.

possess pyrolytic water, which is one of the major drawbacks of the bio-oil produced [49].

3.2.2. Case studies

Korkmaz et al. [65] investigate pyrolysis study with tetra pak which is widely used as an aseptic beverage packaging material. The pyrolysis experiments were carried out in nitrogen atmosphere using a semi-batch pyrolysis reactor with different temperature (400–600 °C). Pyrolysis of wastes yielded the gas and wax besides carbon residue and pure aluminum. The char obtained from pyrolysis was suitable to use as solid fuel because of its high calorific value and low ash content. Gas product was mostly formed from degradation of cardboard and contained the high proportion of carbon oxides.

Balat and Demirbas [66] conducted a laboratory scale experiment to extract pyrolytic oil from black alder wood. An experimental set up for the same is depicted in Fig. 16. They found that the yields of conversion versus time by pyrolysis of black alder wood samples were sharply increased from 10 to 20 min from approximately 23.1 to 66.4%, respectively. While yields of bio-oil versus time by pyrolysis of black alder wood samples were very sharply increased from 10 to 25 min from approximately 9.3 to 36.4%, respectively. The oxygen content is dependent on the bio-oil's water content. Bio-oil without water contains 22–30 wt.% oxygen. It was also observed that the yields of charcoal were 77.2 and 31.4% for 10 and 35 min, respectively.

Chen et al. [67] conducted batch type experiment on biomass pyrolysis/gasification to extract product gas from rice straw and sawdust. Fig. 17 represents experimental setup at laboratory scale which can contain up to 500 g of sawdust fine. They found on economic point of view that the temperature of 700 °C for the cracking reactor is thought to be preferable. The study reveals that product gas production from biomass pyrolysis is sensitive to the operating parameters mentioned above, and the product gas heating value is high, up to 13–15 MJ/Nm^3. It was concluded that a rectangular shape of the pyrolysis reactor is advantageous compared to a cylindrical reactor.

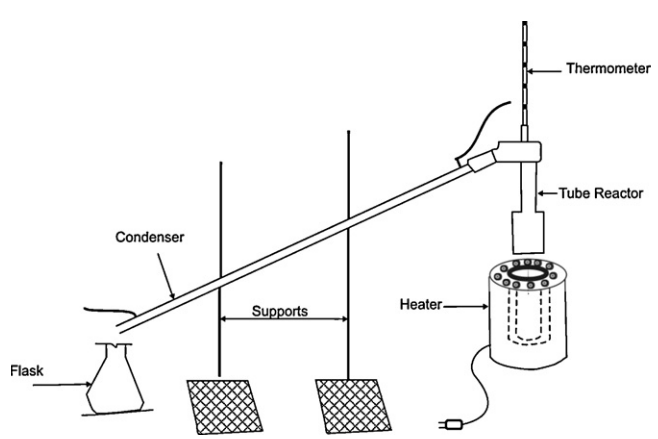


Fig. 16. The schematic view of proposed experiment for pyrolysis oil.

The biomass for entrained-flow gasification needs to be pretreated to considerably increase its heating value and to make it more readily transportable. The pyrolysis temperature had significant effects on composition, structure, heat value of the gaseous, tar liquid and semi-char solid products. It removed most oxygenated constituents of biomass while significantly increased its energy density. The angle of repose, the angle of internal friction of semi-char decrease obviously; the bulk density of semi-char is larger than that of biomass. This could favor the feed of biomass. Considering yield, heating value and transportation characteristics of the solid semichar product, the best pyrolysis temperature was 400 °C and resulting chemical compositions shown is shown in Table 4 [68].

On the early stage similar study was conducted at Georgia Institute of Technology on production of oil from biomass using entrained flow pyrolysis by Kinght et al. [69]. They operate the developed unit at feed rate of 56 kg/h and found mass balance enclosure of 96.8% and mass oil yield was about 41.3%.

An experimental investigation to appraise the pyrolysis characteristics of agricultural residues such as rice straw, sawdust and cotton stalk was carried out by Chen et al. [70]. The end products of such biomass after pyrolysis is mention in Table 5 and it reveals

Table 4
Effect of pyrolysis temperature on chemical composition of the tar product.

Moisture (%)	Pyrolysis temperature (°C)				
	300	400	500	600	700
Moisture	18.10	15.20	33.31	21.00	31.83
Acid	36.24	29.70	30.80	30.47	30.72
Phenol	3.76	4.08	4.61	9.99	4.61
Ketone	8.49	7.01	17.01	6.39	4.61
Alcohol	5.69	6.40	4.77	4.86	5.92
Aldehyde	6.41	–	–	–	–
Ester	–	7.30	3.05	7.83	8.96
Furan	–	1.70	1.83	1.80	3.60
Others	21.58	28.61	4.62	17.66	5.93

Table 5
Product obtained in the fixed-bed reactor (kg/kg biomass).

Biomass types	Gas yield	Tar yield[a]	Water yield	Char yield
Rice straw	0.57	0.03	0.15	0.25
Sawdust	0.64	0.03	0.18	0.15
Cotton stalk	0.58	0.05	0.20	0.17

[a] By difference.

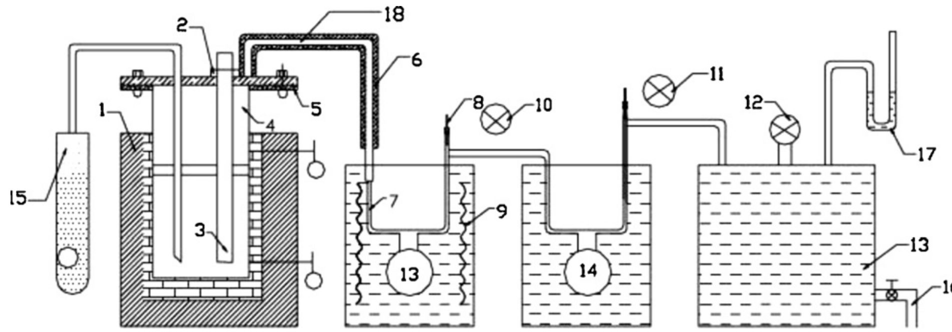


Fig. 17. Laboratory-made batch biomass pyrolysis apparatus.

that the gas yield is sufficiently high for sawdust up to 64 wt.% of the original biomass, for rice straw up to 57 wt.%, while tar is extremely low.

3.2.3. Effect of temperature on feedstock material in pyrolysis process

There are several biomasses considered as feedstock material for pyrolysis and gasification applications. Grape bagasse considered prime feedstock in Turkey. Basically grape bagasse is the residue of wine and juice industry and is used generally as animal feed. Many researcher conducted their study on the conversion of grape bagasse to valuable products by various methods such as pyrolysis [7,71,72]. Recently a study on pyrolysis of grape bagasse was investigated by Demiral and Ayan [73] with the aim to identify optimum process conditions for maximizing the bio-oil yield. They found that the maximum oil yield of 27.60% was obtained at the final pyrolysis temperature of 550 °C, sweeping gas flow rate of 100 cm^3/min and heating rate of 50 °C/min in a fixed-bed reactor. The bio-oils obtained from grape bagasse were offered as an environmentally friendly feedstock candidate for bio-fuels.

Kim et al. [74] pyrolyzed palm kernel shells and determine the influence of reaction temperature, feed size and feed rate on the product spectrum. They reported that maximum bio-oil yield was 48.7 wt.% of the product at 490 °C and maximum yield of phenol plus phenolic compounds amounted to about 70 area percentage at 475 °C. The yield of pyrolytic lignin after its isolation from the bio-oil was approximately 46 wt.%. The effect of temperature on the product distribution is presented in Fig. 18.

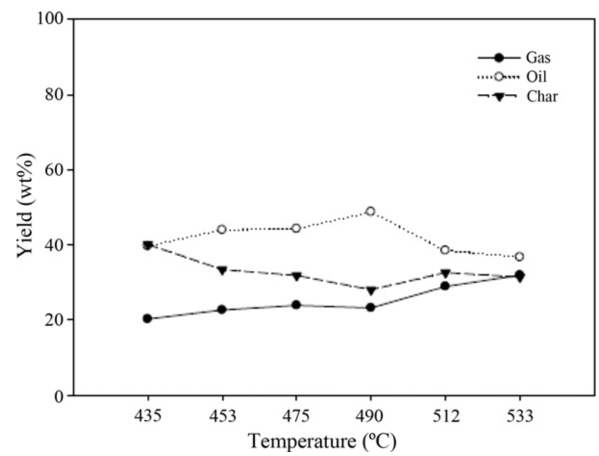


Fig. 18. Effect of reaction temperature on the product distribution.

Harvesting of pyrolysis oil from selected four species (Olive husk, hazelnut shell, spruce wood, and beech wood) at different temperature was analyzed by Demirbas [75]. On the basis of experimental results it was reported that large fraction of the oil is the phenolic fraction, consisting of relatively small amounts of phenol, eugenol, cresols, and xylenols and much larger quantities of alkylated polyphenols. The pyrolysis oil contents and the higher heating values of the oils vary from 32.1 to 49.3% of dry and ash-free basis and from 22.5 to 25.7 MJ/kg, respectively. Fig. 19, reveals the yields of liquid products from the hazelnut shell, olive husk, and beech and spruce wood samples increased from 36.3% to 47.5%, from 38.0% to 48.9%, from 34.8% to 45.4%, and from 32.2% to 43.1% when the pyrolysis temperature was increased from 625 to 800 K and then decreased from 47.5 to 40.0%, from 48.9 to 42.6%, from 45.4 to 37.3%, and from 43.1 to 34.9%, final pyrolysis temperature was increased from 800 to 875 K, respectively.

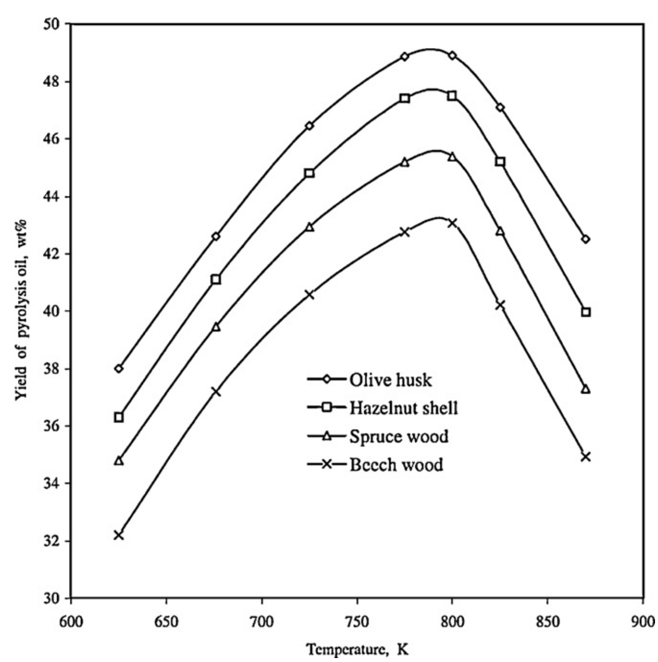


Fig. 19. Influence of temperature on yield of pyrolysis oil.

Commandré et al. [76] pyrolyzed wood in an entrained flow reactor at high temperature (650–950 °C) and under rapid heating

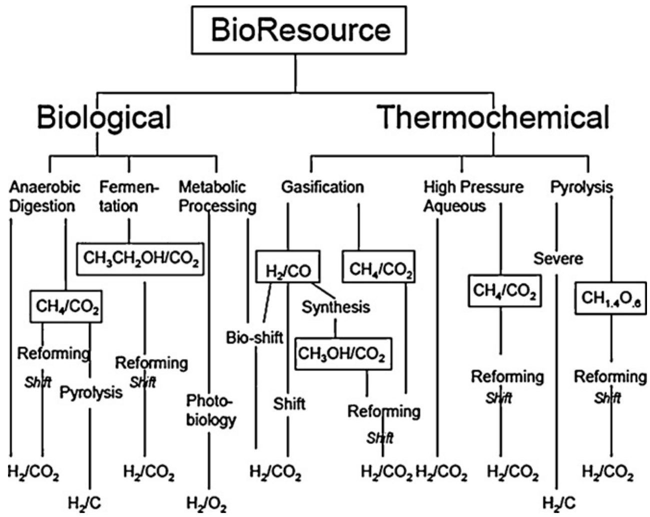


Fig. 20. Pathways from biomass-to-hydrogen.
Source [79].

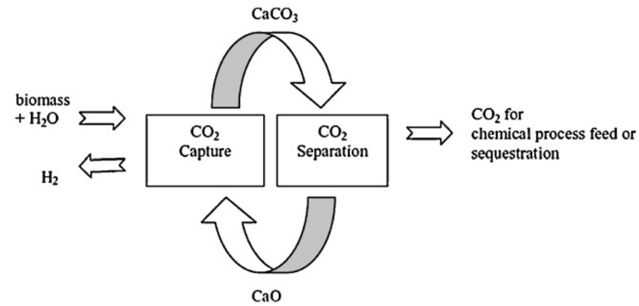


Fig. 21. Hydrogen production through steam gasification of biomass [89].

conditions (>103 K/s). During the experiments particle size kept between 80–125 μm and 160–200 μm. It was elevated that temperature improve hydrogen yield in the gaseous product while CO yield decreases. Under nitrogen atmosphere, after 2 s at 950 °C, 76% (daf) of the mass of wood is recovered as gases: CO, CO_2, H_2, CH_4, C_2H_2, C_2H_4 and H_2O. An experiment performed under steam partial pressure showed that hydrogen production is slightly enhanced.

3.2.4. Potential byproducts: hydrogen

Hydrogen as an energy carrier can play an important role as an alternative to conventional fuels for transportation. It has the highest energy content per unit mass as compared to chemical fuel and can be substituted in place of hydrocarbons in a broad range of applications, often with increased combustion efficiency. Its burning process is non-polluting and it can be used in the fuel cells to produce both electricity and useful heat [77,78]. There are two main routes for biomass-based hydrogen production, namely thermo-chemical and biological conversion routes. Fig. 20 shows the major pathways for hydrogen production from biomass [79]. The thermo-chemical conversion technologies, biomass gasification has attracted the highest interest as it offers higher efficiencies compared to pyrolysis [80–83].

Factors that influence the choice of process are the type and quantity of biomass feedstock [84]. Two types of biomass feedstock are available to be converted into hydrogen [85]: (i) dedicated bioenergy crops, and (ii) less expensive residues/organic waste from regular agricultural farming. The list of biomass feedstocks used for hydrogen production is given in Table 6 [86].

In theme of various objectives, one main objective of the present study are to review the studies conducted on hydrogen production from biomass through thermo-chemical conversion routes (TCCRs) only. The advantage of the TCCRs is that its overall efficiency (thermal to hydrogen) is higher ($\eta = 52\%$) and production cost is lower [87]. The yield of hydrogen that can b produced from biomass is relatively low, 16–18% based on dry biomass weight [88]. TCCRs have three subheadings a pyrolysis, gasification and supercritical water gasification (SCWG) as we already discussed in previous sections. However, hydrogen production from these routes is the part of this specific section. In the pyrolysis process, bio-oil (pyrolysis liquid) is used as a raw material for hydrogen production by the process of steam reforming. It is an endothermic reaction. In the biomass gasification, is also used for cleaner fuel production, biomass is converted completely to CO and H_2 although, practically some CO_2, water and other hydrocarbons including methane also the part of ideal gasification. The char compositions occurred by the fast pyrolysis of biomass can be gasified with gasifying agents for hydrogen. Air, oxygen and steam are widely used gasifying agents.

Table 6
List of some biomass material used for hydrogen production.

Biomass species	Main conversion process
Bio-nut shell	Steam gasification
Olive husk	Pyrolysis
Tea waste	Pyrolysis
Crop straw	Pyrolysis
Black liquor	Steam gasification
Municipal solid waste	Supercritical water extraction
Crop grain residues	Supercritical fluid extraction
Pulp grain residue	Microbial fermentation
Petroleum basis plastic waste	Supercritical fluid extraction
Manure slurry	Microbial fermentation

In the pyrolysis and gasification process, water gas shift is used to convert the reformed gas into hydrogen, and pressure swing adsorption (PSA) is used to purify the product. In order to optimize the process for hydrogen production, a number of efforts have been made by researchers to test hydrogen production from biomass gasification/pyrolysis with various biomass types and at various operating conditions. Florin and Harris [89] investigated steam gasification of biomass, in the presence of a Calcium oxide (CaO) sorbent for CO_2 capture, as a promising pathway for renewable and sustainable production of hydrogen (H_2). Fig. 21 shows the process diagram of study.

On the similar principle a study was conducted in Japan with oak wood for steam gasification using CaO as a CO_2 sorbent by Hanaoka et al. [90] and they reported that H_2 yield increased with increasing reaction temperature. Ahmed and Gupta [91] investigated experimentally main characteristics of gaseous yield from steam gasification. Results of steam gasification were compared to that of pyrolysis. The temperature range investigated were 600–1000 °C. Results of steam gasification were compared to that of pyrolysis at same temperatures. For steam gasification runs, steam flow rate was kept constant at 8.0 g/min. Material destruction, hydrogen yield and energy yield was better with gasification as compared to pyrolysis. This advantage of the gasification process was attributed mainly to char gasification process. A partial overlap existed between gasification and pyrolysis.

Most researchers carried out experiments of hydrogen production with batch-type reactors [90,92,93], circulating fluidized bed reactors [94,95] and bubbling fluidized bed reactors [96,97]. Their studies generally included a main reactor and a gas and tar collecting system. However, some problems were found in these researches: lower hydrogen production and severe tar and char formation. To solve these problems, catalytic treatments as common ways are proposed to reduce tar content in bio-gas and catalysts could be used to effectively eliminate tar in biomass gasification process. The effect of catalyst on gasification products is very

important. The use of the catalyst did not affect the gas yields, but the composition of the gases was strongly influenced. The content of H_2 and CO_2 increased, while that of CO decreased; reduction in content of organic compounds also observed. The increase in hydrogen was probably due to the influence of catalyst on the water gas shift reaction. Dolomite, Ni-based catalysts and alkaline metal oxides are widely used as gasification catalysts [98–100]. A lot of researchers developed different secondary reformers which followed by a gasifier. The reforming of syngas and tar include three methods from a reaction point of view that is steam reforming, catalyst reforming and CO_2 reforming [101]. Similarly, a novel reformer combined with continuous biomass steam gasification was proposed by Ningbo et al. [102] to reform producer gas and crack tars, in which a porous ceramic rather than any catalyst was filled inside the secondary reformer. In the experimental study of biomass gasification (pine sawdust) at different operation conditions has been carried out in an updraft gasifier combined with a porous ceramic reformer. The effects of gasifier temperature, steam to biomass ratio (S/B), and reforming temperature on the gas characteristic parameters were investigated with and without porous ceramic filled in reformer. A high ratio of H_2/CO, ranging between 1.74 and 2.16, can be obtained from product gas porous ceramic reforming. In all cases, the hydrogen concentration shows a clearly increase compared with no reforming process. In addition, reforming temperature showed an important influence on the H_2 production and tars removal. On comparison with no reforming process, the maximum hydrogen content had increased by 45.4% at 800 °C, and the content of TOC dropped from 2348 to 569.7 mg/l.

Other than above discussed two, SCWG also emerging as a new field of hydrogen production because this process can directly deal with high moisture content biomass (>50%). So, biomass drying can be avoided in this area. This factor in the process acts as an advantage in comparison to other processes. In general, properties of water displayed beyond critical point plays a significant role for chemical reactions, especially in gasification process. Here, water is miscible with organic substance above the critical point. One of the key works was on supercritical gasification of wood by Modell et al. [103] and a patent was issued to their work in 1978. They reported the effect of temperature and concentration on the gasification of glucose and maple sawdust in water in the vicinity of its critical state (374 °C and 22 MPa). No solid residue or char was produced. Hydrogen gaseous concentrations up to 18% were observed. Hence, according to above discussed and reviewed research articles, scenario of hydrogen production through biomass using TCCRs can be taken as a long-term transition toward a clean and sustainable energy future. Instead of as a clean fuel with no CO_2 emissions, it can also be used in fuel cells for generation of electricity. Electricity production using a fuel cell is a new alternative for recovering energy from hydrogen.

The hydrogen production through different thermo chemical route of biomass were presented by Wang et al. [104].

$$\text{Pyrolysisofbiomass} \rightarrow H_2 + CO_2 + CO + \text{Hydrocarbongases}$$

$$\text{Catalyticsteamreformingofbiomass} \rightarrow H_2 + CO_2 + CO$$

$$\text{Gasificationofbiomass} \rightarrow H_2 + CO_2 + CO + N_2$$

Hydrogen from organic wastes has generally been based on the following reactions:

$$\text{Solidwaste} \rightarrow CO + H_2$$

$$\text{Biomass} + H_2O + \text{Air} \rightarrow H_2 + CO_2$$

$$\text{Cellulose} + H_2O + \text{Air} \rightarrow H_2 + CO + CH_4$$

3.3. Carbonization

The direct combustion of biomass, though efficient compared to burning of charcoal, is rather inconvenient and polluting because of extensive smoke formation. Charcoal is usually chosen as a fuel because of easier transportability and lower smoke production. In the Indian context presently availability of charcoal in rural areas can make an important contribution to the overall quality of life [105]. The conversion of wood into charcoal is a widespread and long-established craft in developing countries to provide the low-cost fuel for both domestic and industrial markets [106]. It is estimated that in the developing world at least one and a half billion people fulfill their energy needs from wood, either as firewood or indirectly as charcoal [107,108]. Charcoal is usually made from organic matter (biomass) by a carbonization process in which the materials are generally pyrolyzed in charcoal kilns by burning at elevated temperatures of 450–500 °C in the absence of oxygen. Produced charcoal is a solid without toxicity, is stable and not easily decomposed in nature [109]. Lacks of oxygen biomass decompose into a variety of substances the main one of which is charcoal, a black porous solid consisting mainly of elemental carbon. Other constituents are the ash from the original biomass up to 0.5–6% and it depends on the type of biomass to be carbonized. Charcoal can be made from many forms of biomass, including agricultural residues and timber waste [110]. By deploying briquetting process powdery charcoal can be converted into high density energy-concentrated fuel pellets or other different geometric forms [111,112]. Charcoal is also considered as quality fuel for gasification [113].

The charcoal yield at high temperatures and at atmospheric pressure ranging from 36% (dry cellulose substrate) to 40% (45% moisture, dry basis) in the literature [114]. The quality of charcoal depends on both wood species used as a raw material and of the proper application of the carbonization technology [115]. The quality charcoal was characterized by Chaturvedi [116] as follows: It retains the grain of the wood; it is jet black in color with a shining luster in a fresh cross-section. It is sonorous with a metallic ring, and does not crush, nor does it soil the fingers. It floats in water, is a bad conductor of heat and electricity, and burns without flame.

3.3.1. The stages in charcoal formation

Wood undergoes five different temperature stages to converted it into carbon enrich charcoal. Fig. 22 shows different stages of charcoal formation.

3.3.2. Case studies

Charcoal from discarded branches and tops of wood from a Cryptomeria plantation after thinning using a still-operational earthen kiln was produced by Lin and Hwang [117] in Taiwan climatic conditions as shown in Fig. 23. They were found during the study that the recovered fixed carbon reached 33.2%, i.e., one-third of the biomass residual carbon was conserved as charcoal which if left on the forest ground would decompose and turn into carbon dioxide, and based on a net profit of US\$1.13 kg^{-1} for charcoal, an annual net profit of US\$ 14,665 could be realized. They also concluded that charcoaling is feasible alternative to promote reutilization of woody resides which would not only reduce greenhouse gas emissions, but also provide potential benefits to regional economies in developing countries.

Clay and Worrall [118] investigate the scope of carbonization in UK moorland wildfires. They reported the loss of biomass during the fire and associated changes in carbon stocks, black carbon production was approximately 6.35 $g\,cm^{-2}$. Alternatively this is 4.3% of carbon consumed during the fire. By extrapolating this across the Peak District National Park, up to 125 mg of black carbon may be produced per year.

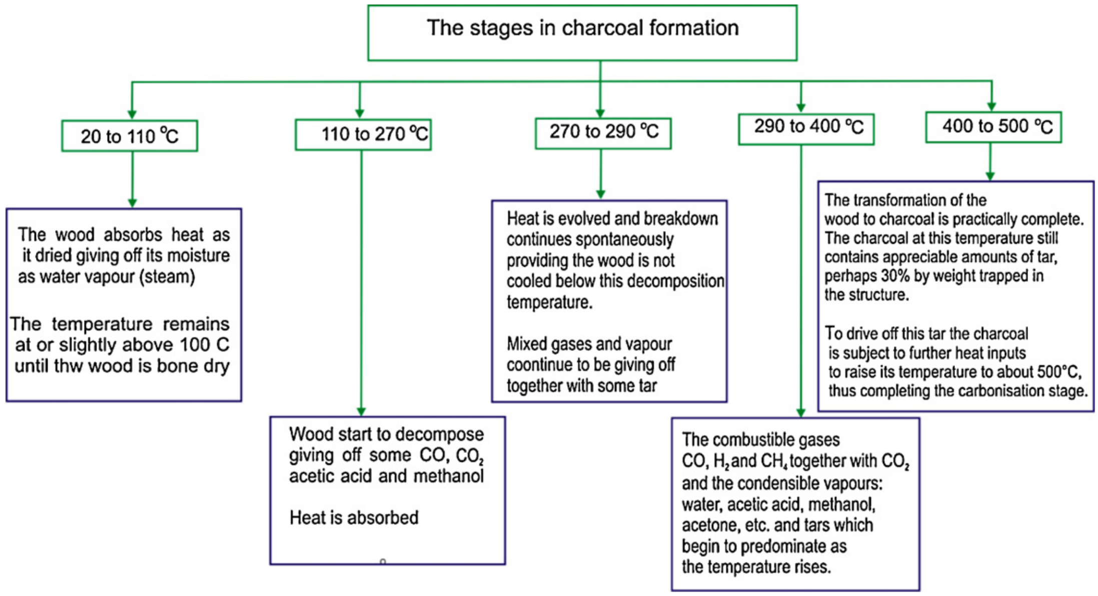


Fig. 22. Stages of charcoal formation.

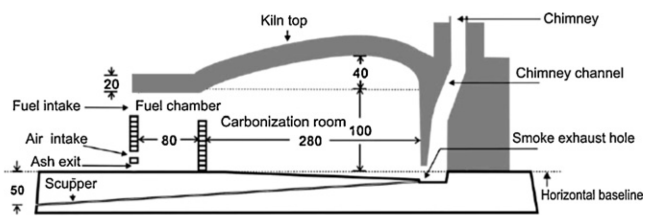


Fig. 23. Earthen kiln for charcoal production.

The climate change mitigation potential of charcoal production in East Africa by examines by Bailis [119]. He found during his study that Kenya is a major charcoal producing region where charcoal is made as a by-product of land clearance for commercial grain production is modeled as the "business-as-usual" scenario. The magnitude of carbon emissions reductions varies depending on land management as well as the choice of carbonization technology. The fixed-land baseline yields annualized carbon emission reductions equivalent to 0.5–2.8 tons per year with no change in production technology and 0.7–3.5 tons per year with improved kilns. In contrast, the baseline defined by the quantity of displaced non-renewable fuel is 2–6 times larger, yielding carbon emissions reductions of 1.4–12.9 tons per year with no change in production technology and 3.2–20.4 tons per year with improved kilns. It was also concluded that, the choice of baseline, often a political rather than scientific decision, is critical in assessing carbon emissions reductions.

An experimental investigation on fixed carbon yield from Thuja wood by two-step isothermal pyrolysis was carried out by Elyounssi et al. [120]. In the first phase (low heating rate and low temperature), where the fixed-carbon increased, corresponded to the decomposition of cellulose and hemicelluloses, while the second phase corresponding to lignin decomposition was marked by the beginning of a decrease in fixed-carbon yield. The maximum value of the fixed-carbon yield obtained with isothermal pyrolysis at 330 °C reached 28.9% as opposed to only 25.5% obtained at 420 °C. It was concluded that by adopting a temperature-time profile composed of a low temperature phase followed by a rapid, high temperature phase to produce charcoal makes it possible to reduce the pyrolysis cycle time while obtaining charcoal of high quality at high yields.



Fig. 24. Improved charcoal kiln built in the Rift Valley, Kenya [121].

Improved charcoal production kiln for developing countries like India and East Africa was designed and developed with the aim to produce charcoal from sustainably managed forests in a more environmentally friendly way (Eco-Charcoal) as shown in Fig. 24. The developed unit is called ICPS (Improved Charcoal Production System). It has a much higher efficiency rating than traditional earth-mound kilns. The efficiency of traditional charcoal production methods is about 10–22% while the efficiency of the ICPS is approximately 30–42%. As compared with traditional carbonization processes, the ICPS reduces emissions to the atmosphere by up to 75%. The ICPS works in two different phases. During the first phase the ICPS works like a traditional kiln where waste wood is burned in a separate fire box to dry the wood and in the second phase of operation the harmful volatiles are burned in a hot 'fire chamber' meaning all resulting emissions are cleaner, minus these already reduced volatiles. The heat gained by flaring the wood gazes, is used and recycled to accelerate the carbonization process. Unlike traditional methods the ICPS can complete a carbonization cycle within 12 h [121].

Khundi et al. [122] examine the relationships among income, poverty and charcoal production in three charcoal-producing districts of western Uganda. Based on their household survey data and propensity score matching techniques they found positive and statistically significant correlations between participation in charcoal-related activities and subsequent household income and poverty levels. Charcoal production was found especially important for households with low agricultural capacity and limited stocks of human and physical capital. They also found that those engaging in charcoal production are not necessarily the poorest cohorts.

4. Conclusions

Looking toward the world energy scenario and from this holistic review. We conclude this paper with following points:

- Downdraft type biomass gasifier was found most appropriate for industrial applications such as heating and drying of agricultural and industrial products.
- Fast pyrolysis is found most suitable for conversion of biomass into liquid fuel and simultaneously it produces gaseous products.
- Bio oil produce through pyrolysis process have chemical properties similar to crude petroleum oil. The refine bio oil can be used as transportation fuel.
- There is huge scope to utilize hydrogen generate during pyrolysis in fuel cell.
- Carbonization of biomass is convert low grade biomass into high grade charcoal fuel. Charcoal is found quality fuels for both updraft and cross draft type gasifier.
- Producing hydrogen by the biomass cannot compete with the well-developed technology for steam-reforming of natural gas. However, an integrated process, in which part of the biomass is used to produce more valuable materials or chemicals and only residual fractions are used to generate hydrogen, can be an economically viable option [123].
- Literatures support that conversion of biomass through thermo chemical conversion path help to protect environment and ecology as well.

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